

Removal behavior of phosphate from aqueous solution by calcined paper sludge

T. Wajima^{a,*}, J.F. Rakovan^b

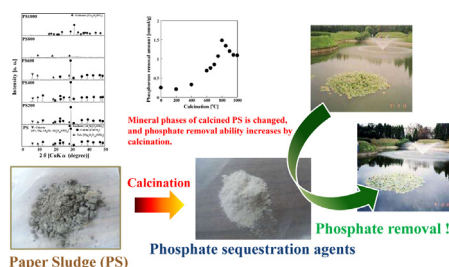
^a Graduate School of Engineering and Resource Sciences, Akita University, 1-1, Tegata-gakuen-cho, Akita 010-8502, Japan

^b Department of Geology and Environmental Earth Science, Miami University, 250 S. Patterson Ave. Shideler Hall, Oxford, OH 45056-2437, USA

HIGHLIGHTS

- ▶ Paper sludge calcined at 800 °C has amorphous phase with high phosphate removal ability.
- ▶ Phosphate removal reaction is an endothermic and spontaneous process.
- ▶ Phosphate removal depends on the formation of calcium phosphate (brushite).
- ▶ Phosphate removal reaction is an endothermic process.

GRAPHICAL ABSTRACT



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ABSTRACT

Paper sludge, which is an industrial waste generated during the manufacture of recycled paper products, was converted into an effective phosphate (PO_4^{3-}) sequestration agent through calcination and its removal behavior toward phosphate ion in aqueous solution was examined. Paper sludge contains mainly cellulose fibers and inorganic fillers together with coating materials such as calcite and kaolinite. The sludge was calcined at temperatures between 200 and 1000 °C for 6 h. Crystalline phases originally present were altered at increasing temperatures (up to 800 °C) in the order kaolinite < calcite. An amorphous phase formed at 800 °C, and gehlenite formed at 1000 °C. Paper sludge calcined at 800 °C (PS-800), which has amorphous phases with high reactivity, removed the greatest amount of phosphate ion. The removal of phosphate by PS-800 was nearly constant in the equilibrium pH range of 5–12, and possessed high selectivity for PO_4^{3-} in solution with coexisting Cl^- , NO_3^- , and SO_4^{2-} . With increasing temperature of the aqueous solution, the kinetics of removal increased and the amount of phosphate removed was greater, which indicated that the removal reaction was an endothermic process. The main process responsible for sequestration of PO_4^{3-} was the formation of brushite [$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$] by the reaction between labile Ca and PO_4^{3-} in the solution.

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1. Introduction

Rapidly increasing production of solid wastes from progressive industrialization is an important environmental problem. The vast amount of paper used in everyday life generates a large amount of waste, 50–60% of which is recycled. During the manufacture of recycled paper, paper sludge is discharged as an industrial waste. More than 3 million tonnes of sludge are

discharged per year in Japan, and approximately 8 and 2 million tonnes are discharged in the United States and the United Kingdom, respectively [1–3]. These amounts are increasing annually. Thus, the paper industry has great impact on the environment due to the quantity of paper sludge generated and disposed. Although a small portion of paper sludge is used as a soil builder and a fertilizer in agriculture [4,5], most paper sludge is disposed of in open dumps or in landfills after incineration. However, the reduction in available landfill space is increasing the costs of land disposal of waste in industrial countries and necessitates other means for the disposal of waste paper sludge. An economically valuable solution to this problem must include utilization of the

* Corresponding author. Tel.: +81 18 889 2748; fax: +81 18 889 2748.
E-mail address: wajima@gipc.akita-u.ac.jp (T. Wajima).

Table 1
Chemical composition of paper sludge (wt%).

Moisture	Organic content	Inorganic content							
		CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	Cl	SO ₃	P ₂ O ₅
4.3	29.0	29.7	15.5	15.6	4.1	0.7	0.1	0.4	0.2

waste materials for new products, instead of disposal in a landfill.

Phosphate is usually considered the limiting nutrient with respect to the eutrophication of natural water bodies. Therefore, water treatment facilities remove phosphate from the wastewater before it is returned to the environment. Various techniques have been used for phosphate removal. Among these, chemical precipitation, adsorption, and biological methods have been applied successfully. Adsorption is a comparatively more useful and more efficient technique for removing phosphate [6].

Because recycling and re-use of wastes are energy efficient, environmentally friendly, and cost-effective, phosphate adsorbents can be produced from many raw materials, such as industrial and agricultural wastes, at low cost. For example, coal fly ash [7,8], slag [9], red mud [10], alum sludge [11], cow bone [12], peat [13], oyster shell [14], scallop shell [15], wheat straw [16], and iron oxide tailings [17] have been used to remove phosphate. Paper sludge varies in composition from mill to mill, but is composed generally of organic fibers (cellulose, hemicelluloses, and/or lignin) and inorganic fillers and coating materials such as kaolinite (Al₂Si₂O₅(OH)₄), limestone (CaCO₃) and talc (Mg₃Si₄O₁₀(OH)₂); the level of potentially toxic components normally is extremely low [18,19]. A previous study confirmed that paper sludge ash, produced from paper sludge by incineration for energy recovery in the manufacturing process, has high affinity for phosphate and heavy metals in aqueous solution [20–23]. In addition, paper sludge calcined at 600–800 °C showed good removal ability for both phosphate ion and heavy metal ions [24,25]. Therefore, paper sludge is expected to have phosphate removal properties after appropriate heat-treatment to develop an active phase for removal. While this sequestration agent is expected to remove phosphate from aqueous solution, more information is required on its properties before it can be widely applied.

The present study describes the formation of phosphate sequestration agent from waste paper sludge by calcination, and the removal behavior of the resulting product toward phosphate ion with the goal of developing original ways of utilizing waste paper sludge.

2. Materials and methods

2.1. Paper sludge and sample preparation

Paper sludge (PS) from a paper company in Japan was used as the starting material. The PS was dried at 80 °C overnight, and sieved for particle size less than 250 μm. The chemical composition of the PS is listed in Table 1. The PS contained 4.3% moisture, organic components such as cellulose fibers (29.0%), and inorganic components (66.7%), predominantly CaO (29.7%), SiO₂ (15.5%), and Al₂O₃ (15.6%). The moisture and organic contents in the PS were determined by differential thermal analysis (DTA)/thermogravimetry (TG) (TG8120, Rigaku, Japan) in the temperature range 20–1000 °C at a heating rate of 10 °C/min in flowing air. The inorganic elements in the PS were determined by X-ray fluorescence (XRF) (Primini, Rigaku, Japan).

PS was calcined at various temperatures from 200 to 1000 °C for 6 h at a heating rate of 10 °C/min in an electric furnace under air atmosphere, and then cooled to room temperature to obtain the sample.

The crystalline phases in each sample were identified by powder X-ray diffraction using monochromated Cu Kα radiation (XRD) (Ultima IV, Rigaku, Japan). The microstructure of these samples was observed by scanning electron microscopy (SEM) (Zeiss Supra 35 VP, Zeiss, Germany).

To determine the phosphate removal ability of each sample, 0.1 g of sample was added into 20 mL of 10 mM NH₄H₂PO₄ in 50-mL polypropylene centrifuge tubes, and the tube shaken using a reciprocal shaker. After shaking for 18 h, the aqueous phase was separated from the solids by centrifugation, and pH of supernatant and the concentration of the phosphate remaining in the supernatant was determined by pH meter (MA-130, Horiba, Japan) and ion chromatography (ICS-3000, Dionex, Japan), respectively. The amount of phosphate ions removed by the sample, *q* (mmol/g), was calculated using the following equation:

$$q = \frac{(C_0 - C) \cdot V}{w} \quad (1)$$

where *C*₀ and *C* are the concentrations (mmol/L) of phosphate ions in the initial solution and at the test time, respectively, *V* is the volume (L) of the solution, and *w* is the weight (g) of the sample added to the solution. It is noted that pHs of the all supernatants after shaking are in the range between 10 and 12 without adjusting pH of the solution.

The soluble amounts of Si, Al, and Ca in PS and the PS calcined at various temperatures were measured as follows: 0.1 g sample was added into 20 mL of 1 M HCl, and the slurry shaken with a reciprocal shaker for 24 h at room temperature. After shaking, the slurry was filtered, and the concentrations of Si, Al, and Ca in the filtrate were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (SPS3000, Seiko, Japan). Soluble amounts of Si, Al, and Ca in sample, *S*, were calculated using the following equation:

$$S = \frac{C \cdot V}{w} \quad (2)$$

where *C* is the concentration (mmol/g) of Si, Al, or Ca ions in the filtrate, *V* is the volume (L) of the HCl solution, and *w* is the weight (g) of the sample added to the HCl solution. It is noted that pHs of all solution after shaking are lower than one.

2.2. Removal experiment

In the present investigation, a batch mode operation was selected to evaluate the removal process. The effect of final pH (3–12), dosage (0–10 g/L), initial phosphate concentration (0–5 mmol/L), contact time (0–120 min), and reaction temperature (10–60 °C) were studied. The experiments were performed on various samples under sufficient duration time (time after equilibrium state). It is noted that there are little difference of analytical values (<5 %) between using centrifugation and filtration.

2.2.1. Solution pH

The effect of pH on phosphate removal was investigated using 1 mM NH₄H₂PO₄ with a final pH in the range of 3–12, due to adjust the solution with initial pH in the range of 1.5–3 using HCl. In each removal study, 0.1 g sample was added to 20 mL solution in 50-mL centrifuge tubes at room temperature and the tube shaken using a reciprocal shaker. After shaking for 12 h, the aqueous phase

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